

LIQUID CRYSTAL DEVICE ALIGNMENT

This invention relates to liquid crystal device alignment.

5 Liquid crystal devices typically comprise a thin layer of a liquid crystal material contained between cell walls or substrates. Optically transparent electrode structures on the walls allow an electric field to be applied across the layer, causing a re-ordering of the liquid crystal molecules.

10 Many different modes of liquid crystal devices are known in the art, for example the twisted nematic device, the cholesteric phase change device, the dynamic scattering device, the supertwisted nematic device and the surface stabilised ferroelectric device modes. It is well known in all of these device modes to provide a surface on the interior walls of the device which will control the alignment of the liquid crystal fluid
15 in close proximity to the surface. For many applications of liquid crystal devices, such a treatment is considered necessary in order to impose a particular configuration on the alignment of the liquid crystal fluid throughout the device and/or to provide an optical appearance in the device which is free of apparent optical defects. The particular significance of this factor for different classes of liquid crystal device is
20 described in greater detail below.

The terms azimuth or azimuthal is used herein to define the molecular (or director \underline{n}) alignment angle movement or energy in the plane of the substrate surface. The terms zenith or zenithal is used herein to define the molecular alignment angle movement or energy in a plane normal to the substrate surface.

In respect of use of nematic and long pitch cholesteric materials for devices known as twisted nematic liquid crystal devices, the relevance of alignment and the problems associated therewith are as follows.

In order to provide displays with a large number of addressable elements it is common to make the electrodes as a series of row electrodes on one wall and a series of column electrodes on the other cell wall. These form typically an x,y matrix of addressable

definitions
azimuth(a)
zenith(a)

Twisted nematic (TN) and phase change devices are switched to an ON state by application of a suitable voltage and allowed to switch to an OFF state when the applied voltage falls below a lower voltage level, i.e. these devices are monostable. For a twisted nematic type of device (90° or 270° twist as in US 4,596,446)[✓] the number of elements that can be rms addressed is limited by the steepness of a device transmission verses voltage curve (as described by Alt and Pleschko in IEEE Trans ED vol ED 21, (1974) P.146 - 155). One way of improving the number of pixels is to incorporate thin film transistors adjacent to each pixel; such displays are termed active matrix displays.

An advantage of nematic types of devices is the relatively low voltage requirements. They are also mechanically stable and have a wide temperature operating range. This allows ^{for the} construction of small and portable battery powered displays. An alternative [^] twisted nematic device is one which is switched from a non-twisted state at zero volts to a twisted state at a higher voltage, as described in GB 9607854.8, which will be referred to in this patent as a VCT device.

One problem with the twisted nematic device is that the contrast ratio of a normally white display remains at a low value until the voltage is increased to a value considerably higher than the threshold voltage. This is due to the nematic material close to the cell walls which does not fully reorient in the applied field due to the strong zenithal anchoring imposed by the surface alignment layer. This lack of surface reorientation also leads to higher voltage operation in the VCT device.

In respect of use of nematic and long pitch cholesteric materials for devices known as bistable nematic liquid crystal devices, the relevance of alignment and the problems associated therewith are as follows.

As described above, twisted nematic and phase change type of liquid crystal devices are switched to an ON state by application of a suitable voltage, and allowed to switch

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to an OFF state when the applied voltage falls below a lower voltage level, i.e. these devices are monostable. An advantage of nematic type of devices is that they have relatively low voltage requirements. They are also mechanically stable and have wide temperature operating ranges. This allows ^{for the} construction of small and portable battery powered displays. A disadvantage of such devices is that their monostable switching characteristic limits the number of lines that can be multiplex addressed.

- Another way of addressing large displays is to use a bistable liquid crystal device. Ferroelectric liquid crystal displays can be made into bistable devices with the use of smectic liquid crystal materials and suitable cell wall surface alignment treatment. Such a device is a surface stabilised ferroelectric liquid crystal device (SSFELCDs) as described by:- L J Yu, H Lee, C S Bak and M M Labes, Phys Rev Lett 36, 7, 388 (1976); R B Meyer, Mol Cryst Liq Cryst. 40, 33 (1977); N A Clark and S T Lagerwall, Appl Phys Lett, 36, 11, 899 (1980). One disadvantage of ferroelectric devices is the relatively large voltage needed to switch the material. This high voltage makes small portable, battery powered displays expensive. Also these displays suffer from other problems such as lack of shock resistance, limited temperature range and also electrically induced defects such as needles.
- If a bistable switching characteristic can be achieved using nematics then a display can be made which has the merits of both the above mentioned technologies but without their problems.

- It has already been shown by Durand et al that a nematic can be switched between two alignment states via the use of chiral ions or flexoelectric coupling: A Charbi, R Barberi, G Durand and P Martinot-Lagarde, Patent Application No WO 91/11747, (1991) "Bistable electrochirally controlled liquid crystal optical device", G Durand, R Barberi, M Giocondo, P Martinot-Lagarde, Patent Application No WO 92/00546 (1991) "Nematic liquid crystal display with surface bistability controlled by a flexoelectric effect".

Patent US 4,333,708 describes a multistable liquid crystal device in which cell walls are profiled to provide an array of singular points. Such substrate configurations

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provide multistable configurations of the director alignments because disclination must be moved to switch between stable configurations. Switching is achieved by application of electric fields.

- 5 Patent Application No.: WO97/14990, (PCT-96/02463, GB95 21106.6) describes a bistable nematic device having a grating surface treatment to at least one cell wall that permits nematic liquid crystal molecules to adopt either of two pretilt angles in the same azimuthal plane. The cell can be electrically switched between these two states to allow information display which can persist after the removal of power.

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Another bistable nematic device is described in GB.2,286,467-A. This uses accurately formed bigratings on at least one cell wall. The bigrating permits liquid crystal molecules to adopt two different angular aligned directions when suitable electrical signals are applied to cell electrodes, e.g. dc coupling to flexoelectric polarisation as described in Patent Application No. WO.92/00546. Since in the two
15 splayed states the director is quite close to being in the plane of the layer, the coupling between director and flexoelectric component can be small, which may hinder switching in some circumstances.

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The bistable nematic device of GB2286467-A also has a further problem which is not present in ferroelectric devices, that is, the need to switch the surface layer of molecules in order to eliminate image sticking effects. Surface layer switching usually requires high voltages which leads to both high power consumption and the need for customised driver circuitry.

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In respect of devices using smectic materials, the relevance of alignment and the problems associated therewith are as follows.

There are a number of devices based on smectic liquid crystal materials including:

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A: Ferroelectric liquid crystals (usually SmC*).

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Bradshaw and Raynes realised that improved SmA alignment for such a device resulted by having a chiral nematic N* phase above the SmA in which the pitch was sufficiently long for the surface forces to cause unwinding of the spontaneous helicity for a significant temperature range above the transition. They also required that the surface should be pre-treated to impart the preferred directions, often by use of parallel or antiparallel rubbing of a polyimide or polyamide layer; GB-2,210,469 USP-4,997,264, GB-2,209,610, USP-5,061,047, GB-2,210,468.

Later it was found that when a bookshelf aligned (where the layer normal is parallel to the plane of the device i.e. $\delta=0$) SmA sample is cooled into the SmC* phase, the layers become tilted in a chevron type of configuration; two type of chevron can exist and are defined as C₁ and C₂ type (ref J.Kanbe et al Ferroelectrics (1991) vol 114, pp3). These are shown in Figure 18. This has been ascribed to the combined effect of shrinkage of the smectic layer spacing and pinning of the layers at the surface. The resulting chevron structure means that the director in the middle of the cell is (roughly) fixed in one of two orientations significantly less than the full cone angle. This means that with no applied field there is a substantial drop in the angle between the optic axis of the two "surface stabilised" states which leads to a corresponding

1 AC field stabilisation:

ordering of words

affect

This geometry has (approximately) the same chevron structure with the director at the chevron interface also at a low angle to the rubbing direction. However, the director at the surface is at a much higher in-plane twist angle due to the competing effects of lying on the SmC* cone and with the preferred alignment pre-tilt. This type of device gives good brightness but suffers from a slower response since it involves surface switching, and from strong surface memory problems which may lead to image sticking.

Two methods may be used to reduce the layer tilt angle and thereby increase the device brightness. Pre-treating the device with a low frequency field of sufficient magnitude or choosing certain materials in which the layer shrinkage on cooling through the smectic phases is reduced (some materials may actually increase layer spacing on cooling). Such a device has similar advantages and disadvantages to the high pre-tilt configurations.

4 Uniform Tilted layer (High pre-tilt anti-parallel) geometry:

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Similar to previous two geometries⁷ but there is no chevron (and therefore no constraint on the director at the cell centre) and the high angle between the bistable states is stabilised solely by the surfaces.

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B: Electro-clinic optical shutters:

Application of a DC field to the smectic A (or other orthogonal smectic) phase of a chiral material leads to an induced tilt of the director and hence optical axis normal to the applied field. In a (approximately) planar aligned liquid crystal cell with electrodes on the substrate surfaces the electroclinic effect induces a rotation of the optic axis by an angle proportional to the applied field E. Thus, an optical shutter with full analogue amplitude or phase modulation may be obtained.

A common problem with such a device is obtaining suitably uniform and planar alignment of the smectic layers. A lesser problem is that the induced switching may involve some rotation of the director away from the preferred alignment direction at the surface. This movement is subject to a surface viscosity which may impede the switching time of the device and also to certain surface memory effects.

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C: Anti-ferroelectric smectic liquid crystals (AFLC):

Certain materials form an anti-ferroelectric phase which may be used in active matrix or direct drive devices. Effectively these devices have a similar appearance to the smectic A phase until sufficient DC voltage is applied, above which the sample is in either of two states (depending on the polarity of the applied signal) similar to the normal ferroelectric phase.

There is a limited number of materials which form this phase (particularly over a wide temperature range) and all those found so far have direct isotropic to smectic phase (i.e. no overlying chiral nematic phase). This means that the materials are more difficult to align, forming batonnets (see Gray and Goodby book) of the smectic at this transition.

normal layer

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15 Bradshaw and Raynes also described a type of device in which the FLC is obtained from cooling directly from the unwound N^* phase in a parallel rubbed device, preferably with in applied DC field applied during the phase transition. The unwound N^* phase has the director in the rubbing directions and on cooling into the SmC^* this orientation is maintained and the layer normal twists through the angle θ . Degeneracy
20 of the direction in which the layer normal is oriented is removed by the application of the DC field.

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Alignment of liquid crystals on a surface is therefore a significant problem for all these device types. Several different means are known by which liquid crystal fluids may be aligned on a surface. Evaporation of silicon monoxide from a direction at least 5 30° from the plane of the substrate provides a surface which aligns a nematic liquid crystal in the plane of the substrate, along an axis orthogonal to the evaporation direction. In contrast, if the evaporation is conducted from a direction making an angle of about 5° or less from the substrate, the resulting surface aligns a nematic liquid crystal along a direction tilted from the plane of the substrate by about 20° in 10 the direction of the evaporation source.

Many commercial liquid crystal devices are fabricated using rubbed polymer alignment layers, especially rubbed polyimide alignment layers. Typically such layers are deposited as an amide precursor polymer by spin deposition of a solution. After 15 removal of the solvent, the polymer coating is imidised by baking at high temperature, then unidirectionally rubbed with a cloth. The resulting surface aligns liquid crystal materials along the direction of rubbing with a tilt out of the plane of the surface in the direction of rubbing. The magnitude of the tilt angle is typically 1° to 2°, but special polyimide formulations and treatments are available which can provide higher 20 magnitudes of pretilt. Some polymer layer⁵ are capable of aligning liquid crystal material when cross linked by exposure to linear polarised light (WO95/22075, GB-9444402516). This avoids the need for rubbing which is useful when substrates carry thin film transistors for a part of active matrix displays. The aligned polymer may also be used in conduction with gratings as noted below. > *conjunction?*

layers

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A further means to provide a surface alignment for liquid crystal materials is available from the deposition of different surfactant materials onto the substrate from solution. A range of different surfactants may be used, including quaternary ammonium salts, alkylated silazenes and basic chromium alkanoates. Treatment of the surface usually 30 entails dipping or spin coating with a dilute solution of the surfactant, and usually results in an alignment of the liquid crystal orthogonal to the plane of the substrate, termed homeotropic alignment. Binuclear chromium alkanoates and other binuclear

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On such a surface the alignment direction is determined by such factors as the flow direction or the direction of a temperature gradient or electric fields at the time the liquid crystal phase first contacts the surface. It is desirable to provide a surface treatment which can allow the liquid crystal alignment direction to rotate freely and repeatedly in the surface plane, but this is not available from known surface treatments.

A second shortcoming of known liquid crystal alignment techniques is that the energy required to change the zenithal angle between the substrate and the liquid crystal director is much greater than the elastic distortion energy of the liquid crystal itself which is generated by commonly applied voltages. This means that in liquid crystal devices using known alignment techniques, the liquid crystal director remains substantially fixed in tilt angle at the cell walls and the switching of the device which provides an optical effect occurs only in the parts of the device which are separated from the cell walls by some distance which depends on the magnitude of the applied field.

• occurring only
• that occurs
• which occurs

The present inventors have found that the above problems are reduced by a surface alignment treatment which allows movement of liquid crystal molecules at or close to the cell walls, hence the liquid crystal director in contact with the wall to reversibly change its orientation at low values of applied field, for example at applied field strengths of the order of less than 1 volt per micron for an applied electric field. The benefits of such a surface treatment may include reduction in the operating voltage of the device and/or an improvement in the switching behaviour of the device such as the electro-optic threshold steepness of the device which determines the amount of information which may be written on an electro-optic display by means of the known methods of RMS multiplex driving.

Accordingly, in a first aspect the invention provides a liquid crystal device comprising a layer of a liquid crystal material contained between two spaced cell wall carrying electrodes structures and an alignment treatment on at least one wall, characterised by means for reducing anchoring energy at the surface alignment on one or both cell walls.

The anchoring energy reduced is one or more of: azimuthal anchoring energy, zenithal anchoring energy, and translational anchoring energy (movement along the alignment treated surface). The significance of anchoring energies in the context of different device types are discussed further below. Further aspects of the invention relevant to specific device types are also discussed further below.

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Anchoring energy arises from surface topography features such as grooves or gratings, and from chemical bonding interactions. The present invention reduces anchoring energy by changing the chemical bonding. Additionally the surface topography may also be changed, for example to reduce the dimensions of grooves or gratings. The means for reducing energy may be an oligomer or short chain polymer which is either spread on the surface or added to the liquid crystal material. The size of oligomer or short chain polymer may be selected to give a desired amount of preferential deposition at cell walls and slight separation from the liquid crystal material host.

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The means for reducing anchoring energy may be an oligomer containing esters, thiols, and/or acrylate monomers and or which is either spread on the surface or added to the liquid crystal material.

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The alignment treatment and means for reducing anchoring energy may be provided by a double layer treatment, now referred to as a substrate layer and a polymer layer. The substrate layer may either be formed in the surface of the cell wall, e.g. by mechanical rubbing of the surface, or (and preferably) be a coating on the cell wall. This coating may include anisotropic features which act to align liquid crystal phases placed in contact with it or in close proximity to it. Such features may include surface relief features including a plain or blazed grating or bigrating structure, or a regular or irregular array of surface features including but not limited to columns, tilted columns, platelets and crystallites e.g. formed by normal or oblique evaporation of inorganic materials onto the surface or by mechanical abrasion or working of the surface. Such features may also include a substantial anisotropy in the substrate formed, for example, by mechanical stretching or rubbing of the substrate layer or by exposure of the substrate layer to polarised actinic radiation.

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The polymer layer (formed on the substrate layer) has the characteristics of having imperfect solubility in the liquid crystal material used in the device, of having a physical affinity for the surface of the substrate, and of retaining a substantially liquid like surface at the polymer/liquid crystal interface.

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The polymer may be applied to the device in various ways. In one approach, the polymer is formed by polymerisation of reactive low molecular weight materials in solution in the liquid crystal fluid. The resulting solution or dispersion of polymer in liquid crystal is then filled into the cell, and the polymer is allowed to coat the substrate surfaces. Optionally, the dispersion of polymer in liquid crystal may undergo intermediate processes such as filtration or centrifuging prior to being filled into the display cell.

In a further approach to applying the polymer to the device the reactive low molecular mass materials may be dissolved into the liquid crystal which is then filled into the display cell. Polymerisation is then initiated by known means, such as by heating or exposure to short wavelength optical radiation in the presence of an initiator. After polymerisation the polymer is allowed to diffuse to and coat the substrate layers.

A still further approach to applying the polymer to the device is provided by polymerisation of the reactive materials in the presence or absence of an inert solvent. The solvent, if present, is removed and the resulting polymer is dissolved in the liquid crystal and filled in to the display cell.

A further approach to applying the polymer to the device is to form the polymer on the substrate by applying a thin layer of reactive low molecular weight materials to the substrate by known means such as by spinning a stoichiometric amount of each onto the substrate in solution in a solvent. After removal of the solvent, polymerisation is initiated by heating or by exposure to light in the presence of a polymerisation initiator. The treated substrates are then assembled into a cell and the liquid crystal added in.

The polymer is characterised in that it is substantially non-crystalline in the presence of the liquid crystal, and that it possesses a glass transition temperature below the operating temperature range of the device. The polymer may be substantially linear in its molecular structure or it may include branch points. The polymer may also be crosslinked to a low degree in order to promote phase separation from the liquid crystal and deposition onto the substrate, but such crosslinking is at such a level that a

fluid, gum-like, gel-like or elastic character is retained, and the polymer does not present a hard glassy or solid like character which is retained on heating.

Preferred polymeric materials include thiol/ene polymers prepared by free radical polymerisation of known monomers in the presence of an added thiol compound which serves to limit the molecular weight of the product through chain transfer reactions. Details of suitable material are listed later.

In relation to twisted nematic devices, the present inventors have found that the contrast ratio of a twisted nematic device can be improved by using an additional surface treatment which reduces the zenithal anchoring energy of the surface and thereby allows field-induced reorientation of the near-surface nematic layers. Such a treatment also has the added advantage of leading to a lowering of the threshold voltage. Lower voltage operation is preferable for both passive matrix and active matrix twisted nematic devices as it allows a display to operate with a lower power consumption.

Accordingly, in a second aspect the invention provides a twisted nematic liquid crystal device capable of being switched from a twisted ~~stated~~ to a non twisted state comprising; two cell walls enclosing a layer of nematic liquid crystal material; electrode structures on both walls for applying an electric field across the liquid crystal layer; a surface alignment on both cell walls providing alignment direction to liquid crystal molecules and arranged so that a twisted nematic structure is formed across the liquid crystal layer at either zero volts or at a higher voltage; means for distinguishing between the two different optical states of the liquid crystal material; CHARACTERISED BY means for reducing zenithal anchoring energy in the surface alignment on one or both cell walls.

Additionally the azimuthal anchoring energy may also be reduced.

The means for reducing azimuthal anchoring energy and zenithal anchoring energy may be an oligomer containing esters, thiol, and/or acrylate monomers either spread

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state

The oligomers may migrate preferentially to the surface in order to minimise the surface free energy. This may dilute the amount of liquid crystal at the surface leading to an effective reduction in the order parameter, S which is defined by (P. G. deGennes, *The Physics of Liquid Crystals*, Clarendon Press, Oxford 1974):

$$S = \frac{1}{2} \langle (3 \cos^2 \theta - 1) \rangle$$

10 Additionally the phase of the liquid crystal material at the surface may be changed by the oligomers, eg from nematic or long pitch cholesteric to isotropic.

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The cell walls may be substantially rigid e.g. glass material, or flexible e.g. polyolefin.

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The electrodes may be formed as a series of row and column electrodes arranged and an x,y matrix of addressable elements or display pixels. Typically the electrodes are 200µm wide spaced 20µm apart.

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Alternatively, the electrodes may be arranged in other display formats e.g. r-θ matrix or 7 or 8 bar displays.

10 In relation to bistable nematic devices, the present inventors have found that the problem of surface layer switching is reduced by using a surface treatment which changes the liquid crystal properties in the vicinity of the surface and so leads to a lower anchoring energy between the liquid crystal and the surface. This allows lower voltage operation without compromising other device parameters.

15 Accordingly, in a third aspect the invention provides a bistable nematic liquid crystal device which comprises; two cell walls enclosing a layer of nematic liquid crystal material; electrode structures on both walls; a surface alignment on both cell walls providing alignment direction to liquid crystal molecules; means for distinguishing between switched states of the liquid crystal material; CHARACTERISED BY means
20 for reducing inelastic azimuthal memory anchoring energy in the surface alignment on one or both cell walls.

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Ideally, the inelastic azimuthal memory anchoring energy is reduced to zero. Preferably, the zenithal anchoring energy is also reduced.

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The means for reducing energy may be an oligomer or short chain polymer which is either spread on the surface or added to the liquid crystal material.

30 Preferably, the oligomer or short chain polymer does not change the pretilt by a substantial amount, e.g. change the pretilt by more than 5°.

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The treatment is used in conjunction with a surface which induces bistable nematic alignment

The bistable surface may be a surface alignment bigrating on at least one of the cell walls that permits the liquid crystal molecules to adopt two different azimuthal alignment directions, as in patent application WO97/14990, (PCT-96/02463, GB95
5 21106.6).

be
The angle between the alignment directions may 90° or less than 90° .
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The grating may be a profiled layer of a photopolymer formed by a photolithographic process e.g. M C Hutley, Diffraction Gratings (Academic Press, London 1982) p 95-125; and F Horn, Physics World, 33 (March 1993). Alternatively, the bigrating may be formed by embossing; M T Gale, J Kane and K Knop, J App. Photo Eng, 4, 2, 41 (1978), or ruling; E G Loewen and R S Wiley, Proc SPIE, 88 (1987), or by transfer from a carrier layer.

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The bigrating may have a symmetric or asymmetric groove profile. In the latter case the surface induces both alignment and pretilt as described in GB2286467-A.

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The gratings may be applied to both cell walls and may be the same or different shape on each wall.
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The bistable surface could alternatively be formed by using an obliquely evaporated material as described in patent Application WO 92/0054 (G Durand, R Barberi, M. Giocondo and P Martinot-Largarde, 1991).

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The cell walls may be substantially rigid e.g. glass material, or flexible e.g. polyolefin.

The electrodes may be formed as a series of row and column electrodes arranged and an x,y matrix of addressable elements or display pixels. Typically the electrodes are
30 200µm wide spaced 20µm apart.

Alternatively, the electrodes may be arranged in other display formats e.g. r-θ matrix or 7 or 8 bar displays.

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5 In relation to smectic devices, the present inventors have found that problems in such devices may be reduced by use of a surfactant to lower the interaction between the surface(s) of cell wall(s) and the liquid crystal in the smectic phase, or in the overlying nematic phase from which the cell is cooled into the smectic phase for all operating temperatures. This use of a surfactant may be termed a slippery surface treatment. Thus improved alignment, optical properties, switching speed and stability to shock of smectic devices are achieved through slippery surface treatment.

10 Accordingly, in a fourth aspect the invention provides a smectic liquid crystal device which comprises: a liquid crystal cell including a layer of smectic liquid crystal material contained between two walls bearing electrodes and surface treated to give both an alignment and a surface tilt to liquid crystal molecules; CHARACTERISED BY means for reducing anchoring energy at the surface alignment on one or both cell walls.

The means for reducing anchoring energy may be an oligomer containing esters, thiols, and/or acrylate monomers and or which is either spread on the surface or added to the liquid crystal material.

20 In its most elemental form the surfactant provides a slippery surface which reduces the interaction between the liquid crystal molecules and those of the surface of the cell wall (or alignment layer surface). Thus, the slippery surface may be thought as having increased freedom for translational and rotational movement of the liquid crystal molecules closest to the surface. There are five surface terms (ref: Int Ferroelectric Liquid Crystal Conf (FLC95), Cambridge, UK, 23-27 July 1995, vol.178 No.1-4 J.C.Jones, pp155-165) which are relevant and may be controlled by the surfactant:

30 (1) α , zenithal anchoring energy. How easily the director surface tilt angle is changed (i.e. a rotational energy).

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(2) β , azimuthal anchoring energy - case of changing surface twist angle of director (i.e. a rotational energy) \odot

(3) γ , related to the pretilt angle of the director at the surface \odot

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(4) Layer pinning term - How easily layers may be moved across the surface (i.e. a translational energy). This is the macroscopic effect of the (partial) adsorption of liquid crystal molecules onto the surface layer reducing translational movement of the molecules and hence of the smectic layers.

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(5) Polar surface energy - In ferroelectrics (or flexoelectrics) a term which is minimum for a particular orientation of the Ps at the surface.

In this aspect of ^{spacing} the present invention each of ^{spacing} these factors is influenced by the presence of a slippery surfactant which acts to separate the solid and liquid crystal regions by the induced changes of liquid crystal order close to the surface. For example, if nematic order exists close to the surface layer of a smectic device, then layer pinning is greatly reduced. If the cone angle is lower, surface switching is reduced as will the polar surface term.

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Advantages provided by this aspect of the present invention are as follows:

- (1) Reduced layer pinning hence control of the smectic layers is easier;
- (2) Reduced nematic-like surface energies, hence orientation changes of the director at the surface are enhanced.
- (3) Reduced adsorption of liquid crystal molecules at the surface, hence reduced surface memory effects and reduced surface viscosity;
- (4) Reduced polarity of the surface, hence less coupling to the spontaneous polarisation coefficient (Ps) in ferro electric liquid crystal systems resulting in less T state formation.

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Specific embodiments of the invention will be described below, by way of example, with reference to the accompanying drawings, in which:

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Figure 1 is a plan view of a matrix multiplexed addressed liquid crystal display;

Figure 2 is the cross section of the display of figure 1;

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Figure 3 shows the configuration for photolithographic exposure leading to the formation of an asymmetric monograting useful in twisted nematic devices.

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Figure 4 shows the transmission versus voltage data for two twisted nematic cells, one of which (dotted line) has been treated with an additive (Norland 65) to give weak anchoring on asymmetric gratings.

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Figure 5 shows the optical contrast ratio versus voltage data for two twisted cells, one of which (dotted line) has been treated with an additive to give weak anchoring.

Figure 6 shows transmission - voltage curves for two voltage controlled twist type cells, one with a standard alignment, the other with a weak anchoring energy treatment.

Figure 7 shows the configuration for photolithographic exposure leading to the formation of a bigrating with orthogonal grating modulations. (C) (C)

Figure 8 shows switching characteristics for two bistable cells, one with standard alignment, the other with a weak surface anchoring energy. (C) (C)

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Figure 9 shows diagrammatically a smectic liquid crystal molecule, and how it moves within a layer when switched to its bistable states in a ferroelectric liquid crystal cell. (C) (C)

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Figure 10 shows variation in memory angle against applied voltage for two bistable ferroelectric liquid crystal devices, one with standard alignment, the other with a weak surface anchoring energy.

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Gratings have been used on both surfaces for alignment. Cell gaps are $2.05\mu\text{m}$ (9)

10 Figure 14 shows the transmission versus voltage data for two cells, one of which (dotted line) has been treated with an additive (MXM035) to give weak anchoring. Gratings have been used on both surfaces for alignment. Cell gaps are 4.6 μ m.

Figure 15 shows the transmission versus voltage data for two cells, one of which (dotted line) has been treated with an additive (MXM035) to give weak anchoring. Rubbed polymer layers have been used on both surfaces for alignment. Cell gaps are 4.6 μ m.

Figure 16 is a diagrammatic view of a bistable ferro electric display with row and column drivers providing an x,y matrix display;

Figure 17 is a cross section of the display cell of Figure 16; and

Figure 18 is a schematic view of a layer of ferro electric liquid crystal material, showing two alignment configurations, the C_1 and the C_2 states.

The application of aspects of the present invention to twisted nematic, bistable nematic, and smectic devices will now be described in separate groups of examples.

30 Twisted nematic devices

The display in figures 1, 2 comprises a liquid crystal cell 1 formed by a layer 2 of nematic or long pitch cholesteric liquid crystal material contained between glass walls

3, 4. A spacer ring 5 maintains the walls typically 2-10 μ m apart. Additionally, numerous beads of the same dimensions may be dispersed within the liquid crystal to maintain an accurate wall spacing. Strip like row electrodes 6 e.g., of SnO₂ or ITO are formed on one wall 3 and similar column electrodes 7 are formed on the other wall 4.

5 With m-row and n-column electrodes this forms an $m \times n$ matrix of addressable elements or pixels. Each pixel is formed by the intersection of a row and column electrode. A row driver 8 supplies voltage to each row electrode 6. Similarly, a column driver 9 supplies voltages to each column electrode 7. Control of applied voltages is from a control logic 10 which receives power from a voltage source 11 and timing
10 from a clock 12.

15 *ner* *side* Either side of the cell 1 are polarisers 13, 13' arranged with their polarisation axis substantially crossed with respect to one another. An additional optical compensator such as a stretched plastic film may also be added between the liquid crystal cell and one of the polarisers. A partly reflecting mirror 16 may be arranged behind the cell 1 together with a light source 15. These allow the display to be seen in reflection and lit from behind in dull ambient lighting. For a transmission device, the mirror may be omitted.

20 Prior to assembly, the cell walls 3, 4 are treated with alignment treatments to provide
a monostable pretilted alignment. The alignment directions R1, R2 are shown as
02 orthogonal to give a 90° or 270° twisted cell, but may be at other angles, e.g., at 45°. Finally, the cell is filled with a nematic material which may be e.g., E7, ZLI2293 or
MLC 6608 (Merck), and may include a chiral additive such as CB15 or R1011
25 (Merck).

In use, the display may be multiplex addressed in a conventional manner by the application of a row waveform applied to each row in turn whilst applying waveforms to all columns. Such addressing is capable of applying two different rms value waveforms at each x,y intersection. One waveform has an rms value above a switching threshold and will therefore switch the liquid crystal material to an ON state. The other resultant waveform has an rms value below the switching threshold and therefore does not switch the liquid crystal material.

The number of x,y pixel elements that can be rms addressed is limited by the steepness of a device transmission verses voltage curve (as described by Alt and Pleshko in IEEE Trans ED vol ED 21, (1974) P.146 - 155). Therefore improvements
 5 to the steepness of the transmission - voltage curve are highly desirable. Additionally, if more of the material can be switched (switching the molecules adjacent a wall surface, rather than switching only at the layer centre) then a higher contrast between ON and OFF states would be obtained.

10 These nematic materials in embodiments of the invention contain the treatment or a precursor of the treatment which leads to a lowering of the anchoring energy.

In general, anchoring of a nematic liquid crystal on a surface can be described by three macroscopic parameters, pretilt, zenithal anchoring energy and azimuthal
 15 anchoring energy. Consider a surface in the x-y plane, parallel to the cell walls. The pretilt (θ_p) is defined as the preferred angle of inclination of the nematic director with respect to the x-y plane. To change the tilt of the surface director from θ_p to an arbitrary tilt θ , an energy per unit area of W must be supplied to the system where [A. Rapini and M. Papoular, J. Phys. (Paris), 36, C-1, 194 (1975)]:

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$$W = W_\theta \sin^2(\theta - \theta_p) \quad (1)$$

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 25 W_θ is the zenithal anchoring energy and represents the energy required in order to change the tilt of the surface director by 90°. If the director has a preferred in-plane orientation, say along the x axis, then an energy must be supplied to the system to change this orientation. The energy is now given by

$$W = W_\phi \sin^2 \phi \quad (2)$$

30 where ϕ is the change in the in-plane orientation and W_ϕ is the azimuthal anchoring energy.

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5 the director at the surface only occurs at high voltages.

[illegible]

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20 pretilt = 5°

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device. Therefore it is clear to see that a surface offering a finite L will lead to a lower voltage, steeper electrooptic response.

Therefore the above modelling has shown that a surface treatment which lowers W_0 will lead to a twisted nematic device which has a lower voltage threshold, a steeper electrooptic response and a higher contrast at a given voltage \odot

Example TN1

An example of a weak anchoring treatment applied to a twisted nematic is now given.

The pretilted alignment surface used in this example was an asymmetric monograting as described in GB 9402492.4; GB-A-2,296,466; WO-95/22078.

The treatment consists of adding a small (1-10%) amount of a UV curing adhesive material to the nematic prior to cell filling. Examples of suitable materials include N65, N63, N60 or N123 (All manufactured by Norland Products Incorporated, North Brunswick, NJ, USA). In this particular example, one of these materials (N65) is used as an additive to the nematic E7 (Merck). This material contains a mixture of esters and acrylate monomers which polymerise under UV radiation.

Before using the N65 additive in a twisted nematic device a set of experiments were carried out in order to show the effect of the N65 treatment on the zenithal anchoring energy, W_0 . This quantity can be calculated by measuring the saturation voltage, V_s . That is, the voltage at which the director tilt in the cell is perpendicular to the surface throughout the thickness of the cell. This can be measured in cells where the surfaces have no preferred alignment direction. In this case flat surfaces of hardbaked photoresist were used (Shipley 1805). This material was spin coated on ITO coated glass to form a $0.55\mu\text{m}$ thick layer. Baking at 160°C for 45 minutes ensured full insolubility in the liquid crystal. When filled with N65/E7 mixtures, these cells show a random Schlieren texture. The saturation voltage was measured by observing when the transmitted intensity of the Schlieren texture falls to zero when viewed between crossed polarisers. W_0 is then given by :

$$W_{\theta} \approx \frac{3.85 \sqrt{\epsilon_0 \Delta \epsilon k_{11}} \cdot V_s}{d} \quad (4)$$

where d is the liquid crystal thickness, k_{11} is the liquid crystal splay elastic constant and $\Delta \epsilon$ is the liquid crystal permittivity anisotropy.

5

Results are shown in table 1. The pure E7 cell failed to show a black state before cell breakdown and so only a lower limit on W_{θ} can be given. In the cases of the E7 containing N65, the curing was performed in a fused silica cell for 10 minutes prior to transferring the mixture to a separate measurement cell. The exposure was carried out using an unfiltered mercury lamp with an optical output of 2.0 mW/cm^2 at a raised temperature of 65°C .

Cell mixture	$W_{\theta} (\text{N m}^{-1})$
Pure E7	$>5 \times 10^{-2}$
2% N65 in E7	6.3×10^{-3}

Table 1

Surface zenithal anchoring energies modified by the presence of N65.

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The above results clearly show that the N65 has reduced the value of W_{θ} in a cell with flat surfaces. The next step is to study the effect of this additive on the operation of a twisted nematic device.

Such a twisted nematic device may employ asymmetric monogratings to induce pretilted alignment and be fabricated in the following way as shown in Figure 3: Shipley 1805 photoresist 20 was spin coated at 3000 rpm onto ITO coated glass 21 for 30 seconds. Next the photoresist layer 20 was baked at 90°C for 30 minutes to remove the solvent. Exposure of the photoresist through a mask 22 was carried out using off axis hard contact photolithography. The mask 22 consisted of a chrome on glass pattern with a pitch of $1 \mu\text{m}$ ($0.5 \mu\text{m}$ gaps and $0.5 \mu\text{m}$ chrome strips). The exposure time was set to 540 seconds with an incident power of 0.15 mW/cm^2 from a mercury

lamp. Development was then carried out in Shipley MF319 for 10 s followed by a water rinse. Samples were finally baked at 160°C for 45 minutes after first receiving a deep UV exposure to preharden the photoresist (3.36 J/cm² at 254nm).

- 5 The above process resulted in a surface monograting with a 1µm pitch and a 0.5µm peak to trough groove depth. The profile is asymmetric (approximately sawtooth in form) which leads to a pretilted alignment if the nematic is under the influence of a bulk twist torque (see GB-A-2,296,466; WO-95/22078). These surfaces were constructed into cells in which the groove direction on one surface was orthogonal to
- 10 the groove direction on the other. The cell gap was set to 2.05µm which corresponds to the first Gooch and Tarry minimum when used with E7 (J. Phys. D. Appl. Phys. vol. 8, p. 1575 (1975)). Filling was then carried out using E7 in the isotropic phase (65°C) followed by slow cooling to room temperature.
- 15 The electrooptic response of cells containing different N65/E7 mixtures was then recorded by placing the twisted nematic cell between crossed polarisers which were oriented parallel to the adjacent grating alignment directions. Transmission was measured using a photodiode with a photo-optic response during the application of a 1kHz sinusoidal drive waveform. Figure 4 shows the transmission versus rms voltage
- 20 for two cells one of which was treated to give weak anchoring. The weak anchoring treatment consisted of adding 2% N65 to E7 and curing for 10 minutes in a pre-cell before transferring the material to the test cell. The data clearly shows that the weak anchoring treatment has lowered the operating voltage. A transmission of 50% of the zero volt value is reached at a voltage of 1.83 V for the weak anchored surface and
- 25 2.13 V for the strong anchored surface. The power consumption of a display can be considered in the most simple case as the power required to charge and discharge a capacitor which is proportional to V². Therefore the weak anchored surface is expected to allow a power saving of roughly 35%.
- 30 The second improvement of the weak anchored cell is the improved optical contrast ratio as shown in figure 5. At 5 V the weak anchored cell has a contrast ratio of 126 while the strong anchored cell has a contrast ratio of 49. At 8 V the difference is even

larger (410 and 74 respectively). Therefore, if a particular application demands a certain contrast ratio then it can be reached at a much lower voltage with a weak anchored surface. The weak anchoring has also lead to a slight increase in the steepness of the electrooptic response. For the weak anchored surface $V_{90} - V_{50}$ is 0.454 V while for the strong surface this quantity is 0.510 V; V_{90} and V_{50} being the voltage at transmissions of 90% and 50% of the zero voltage transmission value respectively.

In summary, the above experimental results have shown qualitative agreement with the theoretical analysis by demonstrating that a surface which has been treated to give a lower W_0 can improve a twisted nematic device. The improvements include a lower voltage threshold, a steeper electro optic response and a higher optical contrast.

Example TN2

In this example MXM035 (Merck) was used as the weak anchoring treatment. The alignment surfaces were asymmetric monogratings as described in example TN1.

The MXM035 consists of two parts which were mixed in equal quantities. This mixture was then added to E7 nematic to give a 4% solution which was cured in a fused silica cell (as described in example TN1) before transferring to a test cell. A measurement of W_0 for the 4% solution revealed a value of $3.85 \times 10^{-4} \text{ J/m}^2$. This is 16 times smaller than the value of measured for N65 (in example TN1). Therefore, the MXM 035 treatment is expected to have a larger effect on the operating behaviour of a TN device.

Cells were constructed using asymmetric monogratings as alignment surfaces. The groove direction on one surface was orthogonal to that on the other to ensure a twisted configuration with a liquid crystal twist of roughly 90° . The cell gap was set to $2.05 \mu\text{m}$ (the first Gooch and Tarry minimum). Figure 13 shows the transmission versus rms voltage for two cells, one of which was treated with 4% MXM035 to give weak anchoring. In this case the weak anchoring treatment has lead to a very large

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0-4 V optical switching times for second minimum TN cells with strong or weak anchoring. .

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Rubbed alignment surfaces were prepared by spin coating a layer of probomide 32 (Ciba Geigy) onto ITO coated glass and baking the substrates at 300°C. The surfaces were then rubbed in one direction by a nylon cloth attached to a rotating roller. Finally cells were constructed in which the rubbing direction on one surface was orthogonal to that on the other. The cell gap was set to 4.6µm using monodispersed spacer beads in the edge seal. Figure 10 shows a comparison of electrooptic responses recorded from two TN cells, one filled with E7 and the other filled with E7+ 4% MXM035. Once again the addition of the weak anchoring treatment has lead to a reduction in operating voltage.

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Example TN4

One particular type of twisted nematic device is the VCT device, which switches from a substantially non-twisted state to a twisted state when a voltage is applied. In this example the operation of the VCT device is improved by the addition of a weak anchoring treatment. The surface alignment in this example was provided by asymmetric grating surfaces as described in example TN1.

The weak anchoring treatment was MXM035 mixed from 10 % of part A and 90% of part B. 4% of this mixture was added to nematic MLC 6608 which has a negative dielectric anisotropy. The MXM035 was then cured by placing the MXM035/MLC6608 mixture in a glass cell and exposing to UV radiation (10 minutes at 2.0mW/cm² while at a temperature of 65°C). After curing, the mixture was used to fill a VCT test cell.

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The VCT cells were constructed so that the grating grooves on one surface were orthogonal to those on the other. Prior to construction the grating on one surface was treated with a chrome complex surfactant in order to induce a homeotropic boundary condition (molecules perpendicular to the wall surface). The grating on the other surface was left untreated in order to induce a planar boundary condition. The cell gap was set to 5.3µm using spacer beads in the edge seal. Figure 6 shows the electrooptic response of two VCT devices, one of which contains the weak anchoring treatment. The VCT containing pure MLC6608 exhibits 50% transmission at a voltage of 2.91 V

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07/24/02 while the VCT containing 4% MXM035 in MLC 6608 exhibits 50% transmission at a voltage of 1.52 V. Therefore, the weak anchoring treatment has lead to a dramatic decrease in operating voltage.

- 5 The dynamic response times of the VCT were measured for these cells for switching between 0 V and 5V as shown in table 3. It can be seen that the addition of MXM035 has lead to a decrease in switch-on time (τ_{on}) and an increase in switch-off time (τ_{off}).

Cell Mixture	τ_{on} (ms)	τ_{off} (ms)
MSc 6608	86	60
MSC 6608	+60	112
4%MXM035		

10 *Table 3*

0-5 V optical switching times for VCT cells with strong or weak anchoring.

- The above examples show that the addition of oligomeric materials (Norland 65, MXM035) into cells with either grating surfaces or rubbed polymer surfaces will lead to a reduction in the operating voltage of a twisted nematic device.
- 15

Bistable Nematic Devices

- These have substantially the same basic construction as shown in Figures 1 and 2, with certain differences. The input polariser is parallel to one alignment state for the case where the alignment states differ in azimuthal angle by 90°. The most significant practical difference is that at least one of the cell walls 3, 4 are treated with alignment gratings to provide a bistable alignment (rather than a monostable alignment as for the twisted nematic case), i.e., two stable alignment directions shown as R,R' 45° apart, but may be 90°. For example, the alignment may be provided by a bigrating with symmetric and asymmetric profiles to give both alignment and a required amount of pretilt. Techniques for producing bigratings to give bistable nematic devices are described in GB-A-2,286,467 (PCT-WO-95/22077) and WO97/14990, (PCT-96/02463, GB95 21106.6).
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The second surface of the cell (if not provided with a bigrating) may be treated with either a planar or homeotropic monostable surface.

- 5 Conventional alignment techniques provide pretilt (zenithal) and alignment direction (azimuthal) with substantial anchoring energy. This means that switching of the device under the influence of electric fields results in movement of the liquid crystal molecules mostly in the centre of the layer, and zero movement at and adjacent the wall surface. Both pretilt and alignment direction are necessary for good device
- 10 performance. What is wanted is pretilt values and alignment together with reduced anchoring energy so that molecules at or adjacent the cell walls can move under the application of normal voltage levels.

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15 ¹ Embodiments of the present invention provides such a wanted pretilt and alignment together with lowered surface anchoring energy. The invention does this, in one embodiment, by inclusion of oligomer units in the liquid crystal layer 2 and which preferentially migrate to the cell wall surfaces.

- 20 Bistable nematic switching relies on surface director reorientation and in order to achieve low voltage switching both the zenithal and azimuthal anchoring energies must be reduced.

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pinning
Furthermore any additional inelastic memory azimuthal anchoring (P. Vetter et al, Euro Display 1993, SID, p.9) due to microscopic absorption of the first nematic layer into the surface must be removed. This anchoring memory may have the effect of pinning molecules in a given position (e.g. between the two switched states) to which they may return after removal of a voltage. Ideally this memory should be completely removed so that the molecules remain in their switched positions after removal of voltages. In practice, reduction rather than complete removal can be satisfactory.

Three examples of the weak anchoring treatment applied to a bistable surface are now given:

Example BN1

The treatment consists of adding a small (1-10%) amount of a UV curing adhesive material to the nematic prior to cell filling. Examples of suitable materials include
5 N65, N63, N60 or N123 (All manufactured by Norland Products Incorporated, North Brunswick, NJ, USA). In this particular example, one of these materials (N65) is used.

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10 In the first experiment this material was added to nematic E7 in concentrations of 1%, 2%, 4% and 6%. The mixture was then used to fill cells whose inside walls were coated with flat polymer layers, without any alignment direction. The purpose of this experiment was to confirm a weakening of the surface anchoring with the addition of N65. Surfaces were prepared using a layer of photoresist (Shipley 1805) which was hardbaked to 160°C to ensure insolubility in the liquid crystal.

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20 Cells were made using these surfaces with a gap of 10µm. Each was filled with a different concentration of N65 including a control sample of pure E7. Filling was carried out in the isotropic phase (65°C) followed by slow cooling to room temperature, and without exposure to UV light. All cells showed a random planar alignment of the nematic which is also called a Schlieren texture. In the case of the pure E7, 1% N65 and 2% N65, the texture could not be moved by applying finger pressure to the cell walls whereas for the 4% and 6% mixtures, the texture was highly mobile and domain walls could be easily moved by applying small amounts of pressure. Once the domain walls had been moved they did not return to their original
25 position but instead remained in the new position for longer than several days. Therefore, the 4% and 6% mixtures lead to a loss of memory anchoring.

A second similar experiment was carried out in which the cells were exposed to UV radiation after filling but before cooling to room temperature. In this case, the 4%, 6%
30 and also the 2% mixtures showed room temperature domain wall mobility. The improvement in the 2% mixture can be explained as follows. The N65 material contains both esters and acrylate monomers which polymerise under UV radiation to form oligomer units which then join together to form larger polymer chains. If the 2%

solution is cured for a short time then the reaction can be terminated when only oligomer units have been formed. The oligomers do not phase separate from the liquid crystal but they so migrate preferentially to the surface in order to minimise the surface free energy. This has the effect of diluting the amount of liquid crystal at the surface which leads to an effective reduction in the order parameter, S which is defined by (P. G. deGennes, The Physics of Liquid Crystals, Clarendon Press, Oxford 1974):

$$S = \frac{1}{2} \langle (3 \cos^2 \theta - 1) \rangle \quad (3)$$

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The reduction in nematic order due to a oligomer concentration has the twofold effect of screening the liquid crystal from the surface which removes the memory anchoring as well as reducing the elastic anchoring energy, W_0 . The uncured material also has this effect but must be added in a greater concentration (>4%) as the acrylate monomer does not preferentially migrate towards the surface.

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The cured material containing 2% N65 was then removed from the cell in which it was cured and used to fill another cell. This second cell also showed a highly mobile Schlieren texture demonstrating that the weak anchoring effect is due to the additive in the bulk as opposed to any surface layer formed during curing.

20

The next set of experiments were designed to show the effect of the N65 treatment on the zenithal anchoring energy, W_0 . This quantity can be calculated by measuring the saturation voltage, V_s as described in example TN1.

25

Results are shown in Table 4. The pure E7 cell failed to show a black state before cell breakdown and so only a lower limit on W_0 can be given. In the cases of the E7 containing N65, the curing was performed in a fused silica cell prior to transferring the mixture to a separate measurement cell. The exposure was carried out using an unfiltered mercury lamp with an optical output of 2.0 mW/cm^2 .

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Cell mixture	Cure time (m)	W_θ (N m ⁻¹)
Pure E7	-	$>5 \times 10^{-2}$
2% N65 in E7	5	5.4×10^{-3}
2% N65 in E7	10	6.3×10^{-3}
2% N65 in E7	30	7.7×10^{-3}
2% N65 in E7+ pure E7 (1:1)	10	8.0×10^{-3}

Table 4

Surface zenithal anchoring energies modified by the presence of N65.

Greater cure times are found to lead to stronger anchoring which is consistent with the formation of longer polymer chains which tend to phase separate from the nematic rather than lower its surface order parameter. One set of data shows that the anchoring energy can also be adjusted by diluting the N65/E7 mixture in pure E7. In all cases the percentage of N65 during the cure process was kept to 2% to ensure consistent reaction kinetics.

The above results confirm that the N65 treatment leads to a loss of in-plane memory anchoring as well as lowering (by about an order of magnitude) the zenithal anchoring energy. The next stage is to test the effect of the treatment on the switching of a bistable nematic device.

One example of a surface which can offer bistable nematic alignment is a surface bigrating (as described in GB2286467-A.) prepared in a manner similar to that shown in Figure 7. In this case samples were made by spin coating 1805 photoresist 20 onto ITO coated glass 21 at a spin speed of 3000 rpm to give a coating thickness of 0.55 μ m. The samples were then softbaked at 90°C for 30 minutes. The bigrating was exposed through a mask 22 using hard contact photolithography (i.e. normal to the mask 22 surface, not at 60° as in Figure 7) with a typical exposure time of 250s (at 0.3 mW/cm²). The mask 22 contained a bigrating pattern of 0.9 μ m chrome squares separated by 0.5 μ m gaps in each direction giving a pitch of 1.4x1.4 μ m. Development was then carried out in Shipley MF319 for 10 sec followed by a water rinse. Samples

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In order to obtain fully selective bistable switching one state has to be favoured by the applied pulse. This can be achieved using dc coupling to a flexoelectric polarisation if the two bistable states have the appropriate pretilts. In WO 92/0054, pretilt can be obtained by using obliquely evaporated SiO.

5

A more controllable method, described in GB2286467-A achieves pretilt by using a bigrating in which both modulations have asymmetric profiles. This method allows a pretilt of typically 17° for one of the bistable states while maintaining a pretilt of 0° for the other state. These surfaces were tested in conjunction with the N65 treatment

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A thin layer 20' of 1805 photoresist was spun onto ITO coated glass 21' as described above. After softbaking, the layer 20' was exposed through the $1.4 \times 1.4 \mu\text{m}$ pitch mask 22' using an off axis diagonal exposure geometry as shown in figure 7; i.e. exposure at about 60° to the surface normal and about 45° to the mask array of square pixels. The exposure time was set to 540 seconds (at 0.15 mW/cm^2). After development and processing the bigrating was constructed opposite a flat photoresist surface (i.e. no grating and hence zero pretilt) using $10 \mu\text{m}$ cell spacers to allow measurement of the surface pretilt at the bigrating surface.

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Table 5 shows the pretilt of the tilted state measured by the crystal rotation method (T. J. Scheffer and J. Nehring, J. Appl. Phys., vol.48, no. 5, p. 1783 (1977)) for cells filled with various mixtures. In all cases the non-tilted state had a pretilt of less than 0.1° .

25

Mixture used to fill cell	Pretilt ($^\circ$)
Pure E7	17.5
2% N65 in E7+ pure E7 (1:1)	17.1
2% N65 in E7+ pure E7 (2:1)	15.4
2% N65 in E7	2.2

Table 5.

Surface pretilt modified by the presence of N65.

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Another example of a weak anchoring treatment was synthesised using block polymerisation of a thiol and a vinyl ether to form the structure A shown below, the subscript n is number of repeats in a chain.



As in example BN1, the precursor materials were added to E7 and then cured in a fused silica pre-cell. The cured mixture was then transferred to a second cell whose inner surfaces were coated with hardbaked photoresist. Filling was carried out at 65°C followed by slow cooling to room temperature. One particular cell was filled with a

A measurement of the saturation voltage revealed that the zenithal anchoring energy had been lowered to a value of $1.2 \times 10^{-3} \text{ N m}^{-1}$. This is even lower than the values shown in table 4 which indicates that the oligomer units formed in this case are more effective at lowering the surface order parameter of the nematic phase. Once again dilution of the 5% solution into pure E7 revealed a regime on grating surfaces in which weak zenithal anchoring was combined with high ($>15^\circ$) pretilt.

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The following structures **B** is a list of example monomers which can also be used to created weak anchoring treatments.

$$\text{HS}(\text{CH}_2)_9\text{SH}$$

NDT (Nonane-1,9-dithiol)B

30 Mixtures of these materials were cured before adding to the liquid crystal and the final mixture was tested in cells containing flat hardbaked photoresist on the inner surfaces

as described in example BN1. Values of W_0 were then obtained using the method described in example BN1.

Of the materials listed, EGTG and NDT are monomers with thiol terminations while HDVE and BVE are difunctional and monofunctional '-ene' materials respectively.

The first set of mixtures studied are shown in table 6. In each case a percentage of monofunctional BVE has been added to the bifunctional HDVE in order to induce chain termination and so form oligomers with smaller molecular weights. In each case the quoted percentage is the molar quantity of BVE with respect to HDVE. Furthermore, the quantity of NDT in each mixture was varied to maintain an equal number of thiol groups and ene groups. To each mixture was added 1% of Igracure 651 (Merck) which acts as a photoinitiator. For each material, curing was carried out under a mercury lamp (2.0 mW/cm^2) for 10 minutes. E7 (Merck) was used as the liquid crystal to which was added 2% of each material (by weight). The results in table 6 show that the resulting zenithal anchoring energy (W_0) lies in the range $3.6\text{--}8.8 \times 10^{-3} \text{ J m}^{-2}$. Therefore, all the mixtures can be considered to be successful in reducing the anchoring from the value found for pure E7 ($>5 \times 10^{-2} \text{ J m}^{-2}$). Furthermore addition of more BVE and hence shorter oligomer chains is found to lead to weaker anchoring.

Material	$W_0 \times 10^{-3} \text{ J m}^{-2}$
NDT / HDVE / 2% BVE	8.8
NDT / HDVE / 5% BVE	5.9
NDT / HDVE / 20% BVE	3.6

Table 6.

Measurement of zenithal anchoring for thiol/diene systems with chain termination.

The correlation of anchoring and molecular length for a given material type was further tested using a set of mixtures containing EGTG, HDVE and BVE. In this case GPC analysis was carried out in order to measure the molecular weights of each

material as shown in table 7; M_n is number average of each chain, M_w is average weight per chain, and W_θ is zenithal anchoring energy. The smallest portion of BVE (2%) is indeed found to lead to the longest molecular weights and vice versa. 1% of each of these materials was added to E7 and W_θ was measured. The correlation of W_θ with molecular weight is fairly good considering the errors in the W_θ measurement.

Material	M_n	M_w	$W_\theta \times 10^{-3} \text{ J m}^{-2}$
EGTG/ HDVE / 2% BE	12640	27330	10.9
EGTG / HDVE / 5% BE	6970	17140	5.3
EGTG/ HDVE / 10% BE	5000	11550	6.6
EGTG/ HDVE / 20% BE	2900	6200	4.4

Table 7.

Measurement of zenithal anchoring for thiol/diene systems with chain termination.

To summarise, in this example, two sets of materials have been studied both have been found to lead to a reduction in W_θ . Furthermore, samples of these materials have also been found to reduce the switching voltages in bistable nematic devices.

Smectic Devices

The display cell 101 shown in Figures 16, 17 comprises two glass walls 102, 103 spaced about 1-6 μm apart by a spacer ring 104 and/or distributed spacers.

Electrode structures 105, 106 of transparent tin oxide are formed on the inner face of both walls. These electrodes are shown as row and column forming an X, Y matrix but may be of other forms. For example, radial and curved shape for a polar coordinate display, or of segments form for a digital seven bar display, or plain sheet electrodes to form an optical shutter.

A layer 107 of smectic liquid crystal material is contained between the walls 102, 103 and spacer ring 104.

Polarisers 108, 109 are arranged in front of and behind the cell 101. Row 110 and column 111 drivers apply voltage signals to the cell. Two sets of waveforms are generated for supplying the row and column drivers 110, 111. A strobe waveform generator 112 supplies row waveforms, and a data waveform generator 113 supplies ON and OFF waveforms to the column drivers 111. Overall control of timing and display format is controlled by a control logic unit 114.

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Prior to assembly, the walls 102, 103 are surface treated by spinning on a thin layer of polymeric material such as polyimide or polyamide, drying and where appropriate curing; then buffing with a soft cloth (e.g. rayon) in a single direction R_1, R_2 . This known treatment provides a surface alignment for liquid crystal molecules. In the nematic and cholesteric phases and in the absence of an applied electric field the molecules at the surface walls 102, 103 align themselves along the rubbing direction R_1, R_2 and at a pretilt angle ξ of about e.g. 2° to 10° to the surface.

The surface alignment treatment is arranged to provide the required value of pretilt ξ . For example, the material polyimide (e.g. Polyimide 32) when rubbed gives a typical pretilt of about 2° ; the actual value depends upon liquid crystal material and the processing. Alternatively, as described in GB-A-2,286; GB-A-2,286,467; GB-A-2,286,894; GB-A-2,2986,893, the cell walls may have formed thereon grating structures which provide a range of pretilt angles and alignment directions. The gratings may be symmetric and/or asymmetric in profile, and shaped to give any desired value of pretilt ξ , and azimuthal and zenithal anchoring energies β, α respectively.

The device may operate in a transmissive or reflective mode. In the former, light passing through the device e.g. from a tungsten bulb 115 is selectively transmitted or blocked to form the desired display. In the reflective mode, a mirror 116 is placed behind the second polariser 109 to reflect ambient light back through the cell 101 and

two polarisers. By making the mirror 116 partly reflecting, the device may be operated both in a transmissive and reflective mode.

Pleochroic dyes may be added to the material 107. In this case only one polariser is needed and the layer thickness may typically be 4-10 μ m.

If the smectic material 107 is a chiral smectic e.g. smectic C (S_C^*) then a bistable device can be made. Such a device is the surface stabilised ferroelectric device (SSFLC) supporting two bistable states which are optically distinct. In a chiral smectic material, molecules tend to lie and move along the surface of an (imaginary) cone as shown in Figure 9. When the surface alignment directions R1, R2 are parallel the (z) axis of these cones are parallel to these alignment directions and the molecules lie either side of the axis on the cone surface.

In one switched state, D1, the molecules lie on one side of the cone, and in the second bistable state, D2, lie on the other side of the cone. The switching is achieved by application of a voltage pulse of appropriate sign and length applied through the electrodes 106, 107 coupling with a spontaneous polarisation coefficient P_s of the material. The cone angle, θ_c , is a function of material parameters. In devices, the molecules in their two switched positions D1, D2, do not lie on the extremities of the cone but some small distance away. This means that the angle between the bistable positions is somewhat less than the cone angle, and can be increased a bit by application of an ac voltage signal to the material; this is known as ac stabilisation mentioned above. Ideally, the angle between the switched states is 45° because this would allow maximum contrast for the cell when arranged between crossed polarisers 108, 109 with the axis of one polariser along one of the switched directions. This gives a dark state in one switched position and a light state in the other switched position.

The angular distance between the two state is defined as the memory angle, θ_m (see N. Itoh et al, Jpn. J. Appl. Phys., 31, L1089 (1992)). The optimum memory angle for maximum brightness in the light state is therefore 45°. However, most materials

A weak anchoring treatment can be added to a ferroelectric to increase the memory angle and so improve the display brightness. This treatment also allows small amounts of translational movement of microlayers formed during cooling from isotropic phases to smectic phases leading to improved alignment.

Example of cell preparation.

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Alignment surfaces were prepared by spin coating a layer of probomide 32 (Ciba Geigy) onto ITO coated glass and baking the substrates at 300°C. The surfaces were then rubbed in one direction R by a nylon cloth attached to a rotating roller. Finally cells were constructed in which the rubbing direction R_1 on one surface was parallel to that R_2 on the other. The cell gap (d) was set to 1.1 μm using monodispersed spacer beads in the edge seal. Each cell was then filled with ZLI 5014 (Merck) ferroelectric liquid crystal doped with small percentages of N65. Before filling the N65 was cured in a separate cell.

Figure 10 shows the memory angle measured from two cells containing either pure ZLI 5014, or 4% N65 in ZLI 5014 as a function of applied voltage (50kHz AC). The results clearly show that the weak anchoring treatment has lead to a significant increase in memory angle at all voltages. Therefore the treatment has improved this ferroelectric device by increasing the on state transmission between crossed polarisers. For example at 5 V, the memory angle has increased from 17.1° to 34.4° which would lead to a device which is 3.7 times brighter.

Bistable ferro electric devices switch upon receipt of a unidirectional pulse of appropriate direction, amplitude, and length. Strobe pulses are applied sequentially down the rows, whilst one of two different data pulses are applied to each column. Examples of addressing are described in USP-5,497,173, GB-2,232,802; US Serial No. 07/977,442, GB-2,262,831.

Several other smectic devices may be made with alignment surfaces of the present invention. For examples ^oelectro-clinic smectic devices; mono stable ferro electric devices USP-5,061,047, USP-4,969,719, USP-4,997,264, colour change smectic projection cells USP-5,189,534, GB-2,236,403. The alignment may produce a chevron type C1 or C2 type of smectic micro layer arrangement; or a tilted bookshelf arrangement where rubbing directions on opposite walls are in the same direction, or real bookshelf alignment.

Reducing anchoring energy allows small amounts of translational movement to occur in micro layers formed during cooling from isotropic phases to smectic phases.

Reduction of anchoring energy can be applied to various smectic devices as follows:

(i). Bookshelf and Quasi-bookshelf with low surface viscosity and no surface memory effects

Most materials used in FLC devices exhibit layer shrinkage on cooling through the SmC* phase due to the increase of the angle between the molecules and layer normal on cooling. The tendency for the pinning of the smectic layers at the surfaces then leads to the formation of a chevron structure.

If the pinning energy is sufficiently high to prevent any translational slippage of the layers (i.e. the energy cost associated with layer slippage is much greater than energies associated with the chevron interface, elastic distortion of the director in the triangular director profile, and the orientational surface energy associated with the director being unable to lie in the preferred alignment direction) the layer shrinking requires that the layers tilt with respect to the surface normal.

If both surfaces have similarly high layer slipping terms then the layers must tilt into a chevron structure which is necessarily symmetric about the central plane of the cell. For typical materials this degree of layer shrinkage is such that the layer tilt angle δ is a constant fraction of the smectic cone angle θ usually about $\delta/\theta = 0.85$. This causes a reduction in the angle between the two bistable states and hence optical contrast in the

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cell. A higher memory angle may be achieved by lowering δ in what is often termed quasi bookshelf geometry. If the layer pinning term is made sufficiently weak (for example a relatively high concentration of the surfactant is used) a bookshelf geometry is obtained i.e. $\delta = 0$. If the azimuthal angle β is also made sufficiently low then a uniform director profile is possible in which the two bistable states are at the optimum angle of $\pm\theta$ to the rubbing direction. The resulting high contrast and brightness of the display is also combined with the other advantages of reduced/no surface memory effects (which would be a problem in other bookshelf devices) and faster response (due to the decoupling of the surface director from the solid surface the surface viscosity becomes equivalent to that of the bulk).

(ii). Chevron with improved memory angle.

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This device uses the slippery surfactant at sufficient concentration to lower layer tilt angle in chevron geometry, thereby leading to a higher memory angle and improved brightness for multiplexed devices. However, it may be possible to lower the orientational surface energies without a strong effect on the translation energy (i.e. layer pinning). Thus, the chevron structure would remain to a large extent (i.e. δ remains unchanged) but the orientation of the director at the surface would be higher. For no applied AC field the surface twist of the director would approach that of the chevron interface. The optical uniformity of this state (and hence contrast) would be improved. Moreover, the lowered surface energy would increase the angle of the director at the surface with an applied AC field, and thus the brightness of an AC stabilised display will also be enhanced.

(iii). Improving isotropic to smectic transition.

Surfactant allows layers to slip easily over the surface to form energy state (i.e. uniform layers) dictated by orientational properties of the surface alone (i.e. no translational restrictions). Particularly useful also in AFLC where N^* (cholesteric) phase is usually not apparent, but also in other devices (e.g., FLC) where stringent material requirements prevent the use of an N^* phase.

(iv)..Improved stability to mechanical, triennial or electrical damage of smectic devices.

Disruption of a well aligned smectic sample through mechanical, electrical or thermal shock leads to pinning of the layers at the surface which is difficult to remove, even though the disrupted state is not the lowest energy state. It the pinning is removed then the system may relax back to this minimum energy state before the disruption.

(v)..Improved high tilt chevron device.

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High surface pre-tilts are used to ensure that the surface orientation of a FLC device in the chevron geometry approaches the cone angle and hence the memory angle is improved (this is used by CANON and is in Jones, Towler Hughes review). In the unwound N* phase the director has a large degree of splay and bend distortion. On cooling into the smectic A phase this bend cannot be supported, due to the presence of the layers and the distortion is pushed to the surfaces where the director is forced to lie away from the desired pretilt. This may lead to variations in the alignment and hence defects in the SmC* phase (until switched this geometry often forms a "sandy texture" on first cooling). Moreover, there may be a plastic change of the pre-tilt caused by the zenithal surface memory effect. This means that when cooled into the SmC* phase the effective pretilt is lowered and the resulting memory angle is reduced somewhat.

With the slippery surfactant, the surface memory is reduced and the pre-tilt remains unchanged. Note, this is an example where the slippery surface technique is used in the nematic phase, but results in improved performance of a smectic device.

(vi). Improved Electroclinic and antiferroelectric (AFLC) devices

In both of these devices, director twist is induced by the DC electric field there is a tendency for the smectic layers to shrink. If pinned at the surface the applied field tends to induce layer tilt, (although in contradiction to the requirement that $E \parallel P_i$) which reduces optical appearance through defects, and may also reduce viewing angle

Advantages ranging from: reduced tendency to form chevron type structure;
reduced surface memory; faster surface switching.

Due to reduced polar surface interaction. This ensures the good optical and electro-optical properties of any of the above devices (in particular the chevron and bookshelf devices).

(ix). Improved alignment of smectic devices.

Treatment prevents defects (for example, pitch lines in overlying N^* phase, or Cl state/zig-zags in SmC^*) from becoming pinned at surface irregularities.

The monomer materials used in embodiments of the invention may include the following, which are given only by way of example:

propane-1,3-diol diacrylate

butane-1,4-diol diacrylate

pentane-1,5-diol diacrylate

hexane-1,6-diol diacrylate

heptane-1,7-diol diacrylate

octane-1,8-diol diacrylate

nonane-1,9-diol diacrylate

decane-1,10-diol diacrylate

glycerol triacrylate

trimethylolpropane triacrylate

pentaerythritol triacrylate
pentaerythritol tetraacrylate
di-pentaerythritol hexaacrylate
ethylene glycol dimethacrylate
1,2-propylene glycol dimethacrylate
propane-1,3-diol dimethacrylate
butane-1,4-diol dimethacrylate
pentane-1,5-diol dimethacrylate
hexane-1,6-diol dimethacrylate
heptane-1,7-diol dimethacrylate
octane-1,8-diol dimethacrylate
nonane-1,9-diol dimethacrylate
decane-1,10-diol dimethacrylate.
glycerol trimethacrylate
trimethylolpropane trimethacrylate
pentaerythritol trimethacrylate
pentaerythritol tetramethacrylate
di-pentaerythritol hexamethacrylate

A further class of polymers includes di-thiol/diene polymers prepared by the copolymerisation of difunctional alkenes with difunctional thiols under free radical conditions. Monofunctional and/or polyfunctional alkenes and/or thiols may be incorporated in order to modify the properties of the polymer, for example to reduce the molecular weight of the polymer or to introduce a controlled degree of crosslinking in the polymer. The following materials given by way of example only may be included in polymers suitable for use in embodiments of the invention:

styrene
ethylene glycol diacrylate
1,2-propylene glycol diacrylate
propane-1,3-diol diacrylate
butane-1,4-diol diacrylate
pentane-1,5-diol diacrylate

hexyl acrylate
heptyl acrylate
octyl acrylate
nonyl acrylate
decyl acrylate
ethyl hexyl acrylate
methyl methacrylate
ethyl methacrylate
propyl methacrylate
butyl methacrylate
pentyl methacrylate
2-methylbutyl methacrylate
hexyl methacrylate
heptyl methacrylate
octyl methacrylate
nonyl methacrylate
decyl methacrylate
ethyl hexyl methacrylate
ethylene glycol divinyl ether
1,2-propylene glycol divinyl ether
propane-1,3-diol divinyl ether
butane-1,4-diol divinyl ether
pentane-1,5-diol divinyl ether
hexane-1,6-diol divinyl ether
heptane-1,7-diol divinyl ether
octane-1,8-diol divinyl ether
nonane-1,9-diol divinyl ether
decane-1,10-diol divinyl ether
glycerol trivinyl ether
trimethylolpropane trivinyl ether
divinyl benzene
butane-1,3-diene
pentane-1,4-diene

hexane-1,6-diol diacrylate
heptane-1,7-diol diacrylate
octane-1,8-diol diacrylate
nonane-1,9-diol diacrylate
decane-1,10-diol diacrylate
glycerol triacrylate
trimethylolpropane triacrylate
pentaerythritol triacrylate
pentaerythritol tetraacrylate
di-pentaerythritol hexaacrylate
ethylene glycol dimethacrylate
1,2-propylene glycol dimethacrylate
propane-1,3-diol dimethacrylate
butane-1,4-diol dimethacrylate
pentane-1,5-diol dimethacrylate
hexane-1,6-diol dimethacrylate
heptane-1,7-diol dimethacrylate
octane-1,8-diol dimethacrylate
nonane-1,9-diol dimethacrylate
decane-1,10-diol dimethacrylate
glycerol trimethacrylate
trimethylolpropane trimethacrylate
pentaerythritol trimethacrylate
pentaerythritol tetramethacrylate
di-pentaerythritol hexamethacrylate
ethylene glycol diallyl ether
1,2-propylene glycol diallyl ether
propane-1,3-diol diallyl ether
butane-1,4-diol diallyl ether
pentane-1,5-diol diallyl ether
hexane-1,6-diol diallyl ether
heptane-1,7-diol diallyl ether
octane-1,8-diol diallyl ether

hexane-1,5-diene	nonane-1,9-diol diallyl ether
heptane-1,7-diene	decane-1,10-diol diallyl ether
octane-1,7-diene	glycerol triallyl ether
nonane-1,8-diene	trimethylolpropane triallyl ether
decane-1,9-diene	di-allyl malonate
ethylene glycol dithioglycollate	di-allyl succinate
1,2-propylene glycol dithioglycollate	di-allyl glutanate
propane-1,3-diol dithioglycollate	di-allyl hexane-1,6-dicarboxylate
butane-1,4-diol dithioglycollate	di-allyl heptane-1,7- dicarboxylate
pentane-1,5-diol dithioglycollate	di-allyl octane-1,8- dicarboxylate
hexane-1,6-diol dithioglycollate	di-allyl nonane-1,9- dicarboxylate
heptane-1,7-diol dithioglycollate	di-allyl decane-1,10- dicarboxylate
octane-1,8-diol dithioglycollate	di-allyl undecane-1,11- dicarboxylate
nonane-1,9-diol dithioglycollate	di-allyl dodecane-1,12- dicarboxylate
decane-1,10-diol dithioglycollate	di-allyl phthalate
glycerol trithioglycollate	butane-1,4-diol di-3-mercaptopropionate
trimethylolpropane trithioglycollate	pentane-1,5-diol di-3-mercaptopropionate
pentaerythritol trithioglycollate	hexane-1,6-diol di-3-mercaptopropionate
pentaerythritol tetrathioglycollate	heptane-1,7-diol di-3-mercaptopropionate
di-pentaerythritol hexathioglycollate	octane-1,8-diol di-3-mercaptopropionate
4,4'-thiobisbenzenethiol	nonane-1,9-diol di-3-mercaptopropionate
di-allyl iso-phthalate	decane-1,10-diol di-3-mercaptopropionate
di-allyl terephthalate	glycerol tri-3-mercaptopropionate
ethane dithiol	trimethylolpropane tri-3-mercaptopropionate
propane dithiol	pentaerythritol tri-3-mercaptopropionate
butane dithiol	pentaerythritol tetra-3-mercaptopropionate
pentane dithiol	di-pentaerythritol hexa-3-mercaptopropionate
hexane dithiol	Also commercial polymers from Norland and Merck eg Norland 65, Norland 63 and Merck MXM035
heptane dithiol	
octane dithiol	

decane dithiol

undecane dithiol

dodecane dithiol

ethylene glycol di-3-

mercaptopropionate

1,2-propylene glycol di-3-

mercaptopropionate

propane-1,3-diol di-3-

mercaptopropionate

2000 2001 2002 2003 2004 2005 2006 2007 2008 2009 2010 2011 2012 2013 2014 2015 2016 2017 2018 2019 2020 2021 2022 2023 2024 2025 2026 2027 2028 2029 2030 2031 2032 2033 2034 2035 2036 2037 2038 2039 2040 2041 2042 2043 2044 2045 2046 2047 2048 2049 2050 2051 2052 2053 2054 2055 2056 2057 2058 2059 2060 2061 2062 2063 2064 2065 2066 2067 2068 2069 2070 2071 2072 2073 2074 2075 2076 2077 2078 2079 2080 2081 2082 2083 2084 2085 2086 2087 2088 2089 2090 2091 2092 2093 2094 2095 2096 2097 2098 2099 2100 2101 2102 2103 2104 2105 2106 2107 2108 2109 2110 2111 2112 2113 2114 2115 2116 2117 2118 2119 2120 2121 2122 2123 2124 2125 2126 2127 2128 2129 2130 2131 2132 2133 2134 2135 2136 2137 2138 2139 2140 2141 2142 2143 2144 2145 2146 2147 2148 2149 2150 2151 2152 2153 2154 2155 2156 2157 2158 2159 2160 2161 2162 2163 2164 2165 2166 2167 2168 2169 2170 2171 2172 2173 2174 2175 2176 2177 2178 2179 2180 2181 2182 2183 2184 2185 2186 2187 2188 2189 2190 2191 2192 2193 2194 2195 2196 2197 2198 2199 2200 2201 2202 2203 2204 2205 2206 2207 2208 2209 2210 2211 2212 2213 2214 2215 2216 2217 2218 2219 2220 2221 2222 2223 2224 2225 2226 2227 2228 2229 2230 2231 2232 2233 2234 2235 2236 2237 2238 2239 2240 2241 2242 2243 2244 2245 2246 2247 2248 2249 2250 2251 2252 2253 2254 2255 2256 2257 2258 2259 2260 2261 2262 2263 2264 2265 2266 2267 2268 2269 2270 2271 2272 2273 2274 2275 2276 2277 2278 2279 2280 2281 2282 2283 2284 2285 2286 2287 2288 2289 2290 2291 2292 2293 2294 2295 2296 2297 2298 2299 2300 2301 2302 2303 2304 2305 2306 2307 2308 2309 2310 2311 2312 2313 2314 2315 2316 2317 2318 2319 2320 2321 2322 2323 2324 2325 2326 2327 2328 2329 2330 2331 2332 2333 2334 2335 2336 2337 2338 2339 2340 2341 2342 2343 2344 2345 2346 2347 2348 2349 2350 2351 2352 2353 2354 2355 2356 2357 2358 2359 2360 2361 2362 2363 2364 2365 2366 2367 2368 2369 2370 2371 2372 2373 2374 2375 2376 2377 2378 2379 2380 2381 2382 2383 2384 2385 2386 2387 2388 2389 2390 2391 2392 2393 2394 2395 2396 2397 2398 2399 2400 2401 2402 2403 2404 2405 2406 2407 2408 2409 2410 2411 2412 2413 2414 2415 2416 2417 2418 2419 2420 2421 2422 2423 2424 2425 2426 2427 2428 2429 2430 2431 2432 2433 2434 2435 2436 2437 2438 2439 2440 2441 2442 2443 2444 2445 2446 2447 2448 2449 2450 2451 2452 2453 2454 2455 2456 2457 2458 2459 2460 2461 2462 2463 2464 2465 2466 2467 2468 2469 2470 2471 2472 2473 2474 2475 2476 2477 2478 2479 2480 2481 2482 2483 2484 2485 2486 2487 2488 2489 2490 2491 2492 2493 2494 2495 2496 2497 2498 2499 2500 2501 2502 2503 2504 2505 2506 2507 2508 2509 2510 2511 2512 2513 2514 2515 2516 2517 2518 2519 2520 2521 2522 2523 2524 2525 2526 2527 2528 2529 2530 2531 2532 2533 2534 2535 2536 2537 2538 2539 2540 2541 2542 2543 2544 2545 2546 2547 2548 2549 2550 2551 2552 2553 2554 2555 2556 2557 2558 2559 2560 2561 2562 2563 2564 2565 2566 2567 2568 2569 2570 2571 2572 2573 2574 2575 2576 2577 2578 2579 2580 2581 2582 2583 2584 2585 2586 2587 2588 2589 2590 2591 2592 2593 2594 2595 2596 2597 2598 2599 2600 2601 2602 2603 2604 2605 2606 2607 2608 2609 2610 2611 2612 2613 2614 2615 2616 2617 2618 2619 2620 2621 2622 2623 2624 2625 2626 2627 2628 2629 2630 2631 2632 2633 2634 2635 2636 2637 2638 2639 2640 2641 2642 2643 2644 2645 2646 2647 2648 2649 2650 2651 2652 2653 2654 2655 2656 2657 2658 2659 2660 2661 2662 2663 2664 2665 2666 2667 2668 2669 2670 2671 2672 2673 2674 2675 2676 2677 2678 2679 2680 2681 2682 2683 2684 2685 2686 2687 2688 2689 2690 2691 2692 2693 2694 2695 2696 2697 2698 2699 2700 2701 2702 2703 2704 2705 2706 2707 2708 2709 2710 2711 2712 2713 2714 2715 2716 2717 2718 2719 2720 2721 2722 2723 2724 2725 2726 2727 2728 2729 2730 2731 2732 2733 2734 2735 2736 2737 2738 2739 2740 2741 2742 2743 2744 2745 2746 2747 2748 2749 2750 2751 2752 2753 2754 2755 2756 2757 2758 2759 2760 2761 2762 2763 2764 2765 2766 2767 2768 2769 2770 2771 2772 2773 2774 2775 2776 2777 2778 2779 2780 2781 2782 2783 2784 2785 2786 2787 2788 2789 2790 2791 2792 2793 2794 2795 2796 2797 2798 2799 2800 2801 2802 2803 2804 2805 2806 2807 2808 2809 2810 2811 2812 2813 2814 2815 2816 2817 2818